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PHASE STABILITY AND MECHANICAL PROPERTIES OF C-22 ALLOY AGED IN THE TEMPERATURE RANGE 590 TO 760°C FOR 16,000 HOURS

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ABSTRACT

The phase stability of C-22 alloy (UNS #N06022) was studied by aging samples at 593, 649, 704 and 760°C for 2000 h (2.7 mo) and 16,000 h (1.8 yr). The tensile properties and the Charpy impact toughness of these samples were measured in the mill annealed condition as well as after aging. The microstructures of samples aged 16,000 hours were examined using scanning and transmission electron microscopy (SEM and TEM). Preliminary TEM results suggest that μ phase forms at all temperatures investigated. Discrete carbide particles in addition to a film with very uniform thickness which appears to be μ phase formed on grain boundaries in the sample aged at 593°C. The ordered Ni_2(Cr, Mo) phase was also seen in this sample. At the higher aging temperatures, mainly μ phase forms covering all the grain boundaries and also distributed throughout the bulk. Although strength increased somewhat with aging, the ductility decreased due to the formation of these grain boundary precipitates and brittle intermetallics.

INTRODUCTION

Nickel-base alloys containing high concentrations of chromium (Cr) and molybdenum (Mo) are being considered as possible materials for fabrication of high-level radioactive waste disposal containers which will be required to contain the waste for at least 10,000 years. Heat generated by radioactive decay of the waste is expected to initially raise the temperature of the disposal container to as high as 200°C. The temperature will then gradually drop over a period of several thousand years. Although these temperatures are generally considered low for most engineering applications, the times involved are very long. Consequently, one area of concern is phase stability of the disposal container materials since the precipitation of deleterious phases over such long times can affect the corrosion resistance and/or the mechanical properties of an alloy. Aging studies such as the one presented in this paper will be used to determine which phases might form in candidate materials and the kinetics of transformation so that predictions may be made as to which phases will form under repository conditions.

Several phases are known to form in Ni-Cr-Mo alloys. In the temperature range used in this study, primarily μ phase (a Mo-rich, rhombohedral phase with lattice parameters a = 9.04 Å and α = 30.5°[1]) is reported [2-6]. Because μ is Mo rich, there is evidence that Mo-depleted zones around μ phase particles will lead to localized corrosion attack [2-4,6]. At temperatures below approximately 600°C, an ordered Ni_2(Cr,Mo) phase also forms [4,6,7]. This phase has a Pt_2Mo type structure and is evidenced by superlattice reflections at the 1/3 <220> or 1/3 <420> positions in the Ni-rich matrix electron diffraction patterns [8]. This ordered phase has been suspected of increasing the susceptibility of Ni-Cr-Mo alloys to hydrogen embrittlement and stress corrosion cracking [4]. Two other intermetallics have been seen in Ni-Cr-Mo alloys similar to C-22: P phase (orthorhombic with a=16.983, b=4.752 and c=9.07 Å [1]) and σ (tetragonal with a=8.80 and c=4.54 Å [1]). Leonard [2] found that a uniform film of P phase formed at grain boundaries in the early stages of aging alloy C-276 (Ni-16% Cr-16% Mo-4% W-5% Fe, low C and Si), and this phase later transformed to μ. At higher temperatures, a more particulate film (composed of discrete particles) formed on grain boundaries. Sigma and P have not been seen in C-22 except in the as-welded condition [9].

Mechanical and corrosion properties have been measured in similar alloys as a function of aging time. Matthews [10] aged several Ni-Cr-Mo alloys at temperatures between 650 and 870°C for times up to 8000 h. He found that alloys S (Ni-16% Cr-15% Mo) and C-4 (Ni-16% Cr-16%

Mo), both with low C, W and Fe, showed increased strength after aging at temperatures around 590°C. The room temperature tensile elongation in both cases remained above 70% of the unaged value even in the strongest samples. Formation of the ordered $Ni_2(Cr,Mo)$ phase was responsible for the increase in strength and had the greatest effect on the elongation. It was only seen, however, at the lower aging temperatures (540 and 590°C in alloy S and C-4 and at 650°C in C-4). A decrease in Charpy impact toughness was also seen in these samples where ordering was observed, but μ phase which formed in C-4 at 760°C was much more detrimental to impact toughness. At 870°C, μ phase was also seen in C-4, but it formed in larger more uniformly distributed particles which did not reduce the ductility of the alloy. A similar effect of μ phase precipitation on properties was reported by Tawancy [5], but he did not see μ phase in alloy C-4. The reported alloy C-4 compositions[5,10] were nearly identical except for 1% more Cr in the alloy that did not form μ phase [5]. An increase in strength accompanied by a moderate decrease in tensile elongation with the formation of $Ni_2(Cr,Mo)$ has also been reported in alloys C (Ni-15.5% Cr-16% Mo-4% W-6% Fe, higher C and Si) and C-276 [4]. In 1998, Rebak et al. [7] reported that C-22, C-4 and C-276 aged at 427°C for times up to 40,000 h showed negligible strengthening but some reduction in the ductility measured in a uniaxial tension test. This decreased ductility was attributed to the early stages of $Ni_2(Cr,Mo)$ precipitation.

EXPERIMENTAL

Two heats of C-22 alloy (Heat #1: 0.29Al, 0.003C, 1.74Co, 21.10Cr, 4.7Fe, 0.010Mg, 0.21Mn, 13.50Mo, 0.02N, 55.67Ni, 0.023Si, 0.12V, and 2.90W; Heat #2: 0.25Al, 0.002C, 1.56Co, 21.60Cr, 4.3Fe, 0.017Mg, 0.24Mn, 13.50Mo, 0.04N, 0.05Nb, 55.33Ni, 0.006P, 0.003S, 0.037Si, 0.15V, and 3.00W, all in wt.%) in the form of 1/2" thick plate were aged for 2000 and 16,000 h at 593, 649, 704 and 760°C. The aging was done in air, and the temperature was maintained to within ±6°C. Specimens in the mill-annealed as well as in the aged condition were tested in tension at room temperature according to ASTM Specification E8 using standard round bar specimens with 0.25-inch diameter in the gage section. The strain was measured using an extensometer over 1 inch of the gage section. Charpy impact testing was done at room temperature according to ASTM Specification E23 using full-size standard V-notch specimens. Samples were prepared for metallographic examination using standard polishing techniques and an electrochemical etch in a solution of 5 g oxalic acid in 95 cc of 37% HCl solution at 6 V for only a few seconds. Samples for TEM were mechanically thinned to 175-200 μm followed by jet polishing in a 5% perchloric - acetic acid solution at room temperature and 40 - 60 V. Additional samples without preferential etching of second phases were prepared by dimpling and ion milling. The foils were examined in a JEOL JEM-200CX TEM operated at 200 kV. Only samples from heat #1 aged for 16,000 h were examined.

RESULTS

The results of mechanical testing are given in Table I. All values represent the results of at least two tests. The yield strength is plotted in Figure 1 as the ratio of the strength of the aged specimen to that of the unaged, mill annealed specimen. In most cases some strengthening has occurred. The samples aged at 593 and 649°C, show little change in strength after a 2000 h exposure, but some strengthening occurs at 704 and 760°C. After 16,000 h, strengthening has occurred at all temperatures with the greatest increase occurring at 704°C.

As shown in Figures 2 and 3, this strengthening has occurred at the expense of the ductility. Aging at 593°C for 2000 h does not affect either the elongation or the Charpy impact toughness, but both decrease rapidly as the aging temperature is increased. The sample aged at 593°C for 16,000 h retained about 70% of its elongation, but the Charpy impact toughness dropped to less than 20% of the value for mill annealed samples. At higher aging temperatures, the elongation drops rapidly, and the Charpy impact toughness drops to very low values.

Table I

Mechanical Properties of Aged C-22 Alloy

Heat #	Temp. (°C)	Time (hours)	UTS (MPa)	0.2% Yield (MPa)	% Elong.	%RA	Charpy V-Notch (J)
1	As-annealed	0	767.4 768.8	339.9 353.7	66.2 66.6	76.1 78.4	357 357
2	As-annealed	0	756.4 752.9	342.0 341.3	70.0 70.0	77.0 77.8	357 357
1	593	2000 16000	765.3 806.0	334.4 380.6	67.6 55.4	77.9 50.7	357 72
2	593	2000 16000	765.3 930.8	360.6 484.7	68.3 39.0	72.3 31.1	357 37
1	649	2000 16000	710.2 906.7	323.4 482.6	62.2 25.5	58.3 22.2	236 26
2	649	2000 16000	755.0 808.8	352.3 464.0	61.6 18.1	51.0 17.4	134 18
1	704	2000 16000	835.7 967.4	391.6 634.3	39.6 4.9	30.9 5.4	30 3
2	704	2000 16000	771.6 875.7	377.8 577.8	35.0 3.1	- 1.3	22 3
1	760	2000 16000	914.2 911.5	466.1 533.0	14.4 4.7	10.3 5.7	9 3
2	760	2000 16000	828.8 803.3	446.8 535.7	12.4 3.6	10.5 1.5	7 3

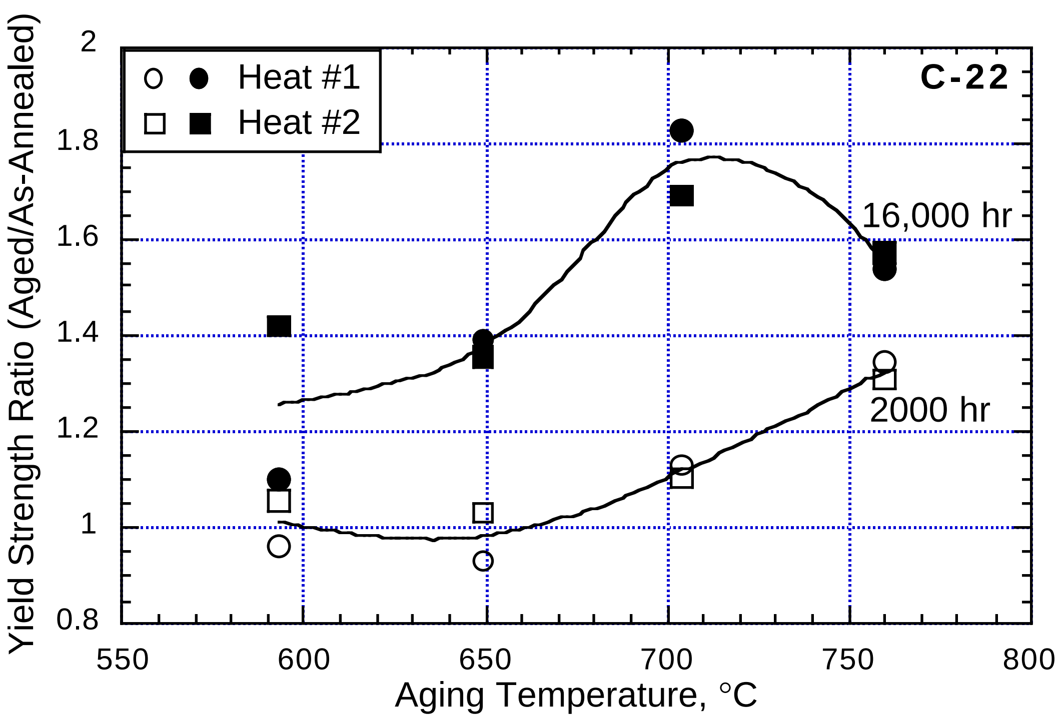


Figure 1. The effect of aging temperature on the yield strength of C-22 alloy.

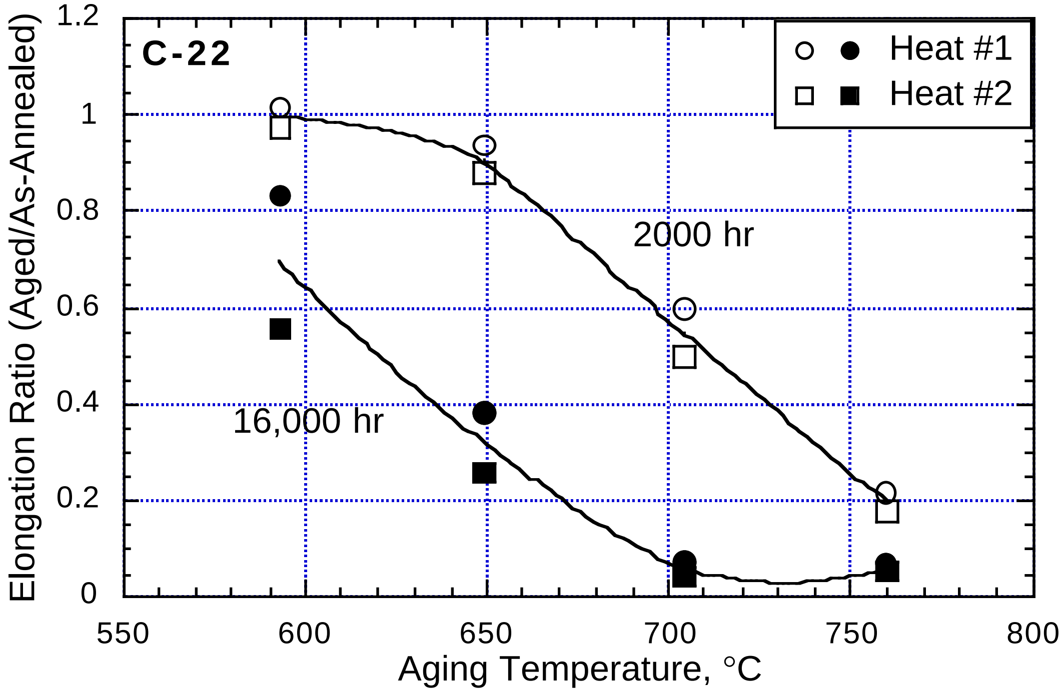


Figure 2. The effect of aging temperature on the total elongation (in 1 inch) of C-22 alloy.

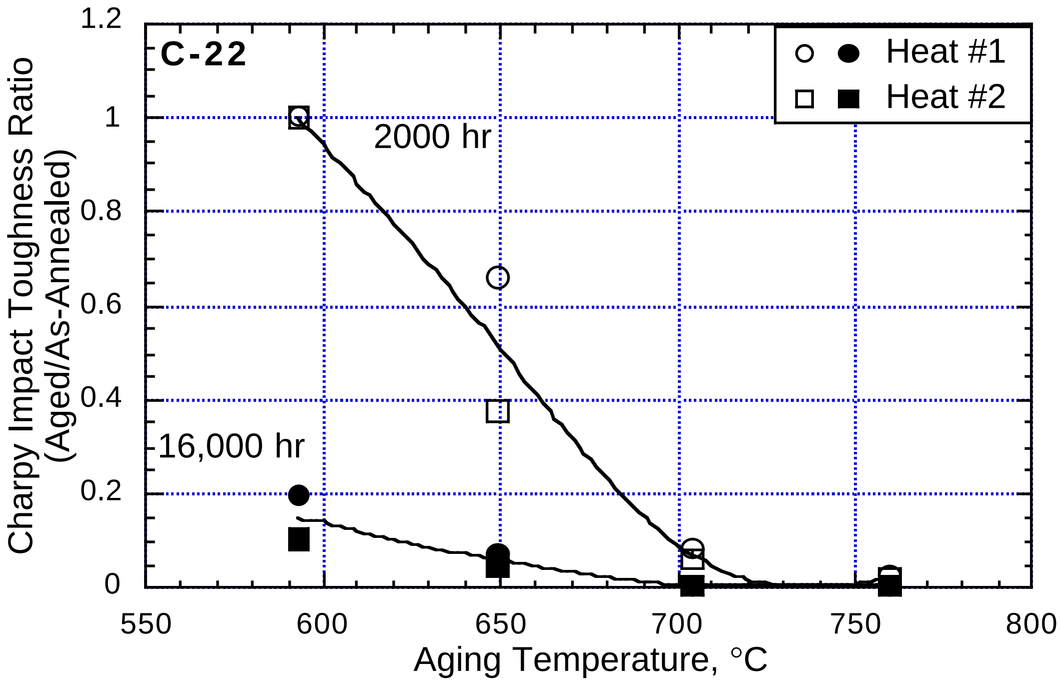


Figure 3. The effect of aging temperature on the Charpy impact toughness of C-22 alloy.

In the mill annealed condition, C-22 is a face-centered cubic (fcc) solid solution with a few, primarily M_6C, carbides distributed throughout the fcc matrix. Figure 4 shows SEM micrographs of the samples from heat #1 aged for 16,000 h. In the sample aged at 593°C, precipitation has occurred at most of the grain boundaries. The interior of the grains, however, is nearly as free of precipitation as those of mill annealed samples. In the sample aged at 649°C, more precipitation has occurred, but it is concentrated near grain boundaries. Some grain boundaries have a very uniform film and others are covered with discrete particles. At 704 and 760°C, more precipitation occurs within the grains as well as on the grain boundaries.

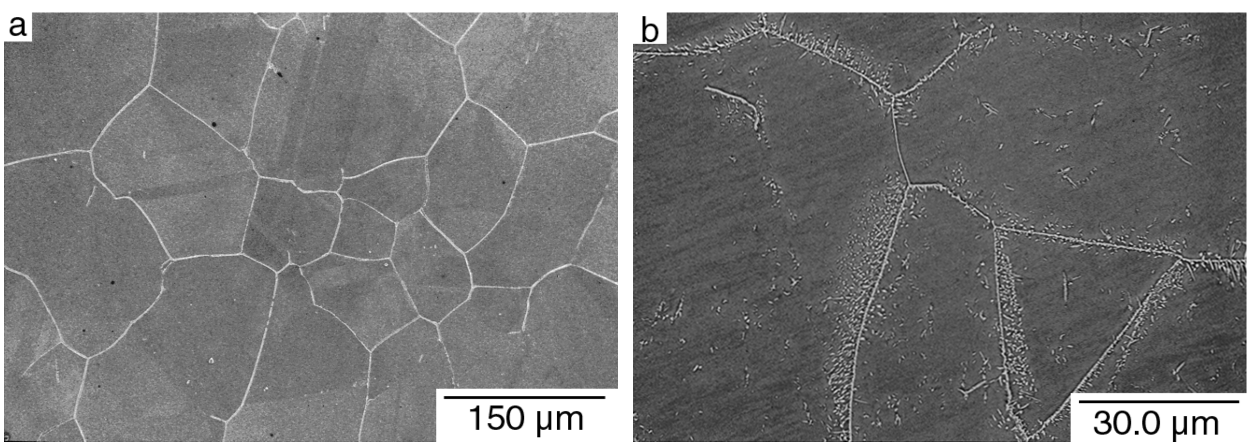
The results of TEM characterization are still preliminary, but sample micrographs are shown in Figures 5 and 6. At 593°C, the thin, uniform grain boundary film which forms (Figure 5a) is highly faulted. The phase growing out from the boundary has not yet been identified. At least in some areas, the more particulate grain boundary precipitates (Figure 5b) are carbides as determined by selected area electron diffraction. Due to the similarity in the structures of M_6C, $M_{12}C$ and $M_{23}C_6$, however, the type of carbide that forms was not determined. The mottled appearance within the grains of Figures 5a and b is due to $Ni_2(Cr, Mo)$ precipitation which was identified by its characteristic superlattice reflections at 1/3 <220> positions.

In the sample aged at 760°C, most of the particles formed after 16,000 h are μ phase. These are the dark particles in Figure 6 (right). The larger, light grain boundary phase in this figure was not as abundant as μ and has not been conclusively identified. Several electron diffraction patterns could be indexed self consistently for a tetragonal structure. The lattice parameters which gave the best fit were a=8.7 and c=5.9 Å. This structure is very close to sigma phase, but the lattice parameters are somewhat different. Qualitative Energy Dispersive Spectroscopy (EDS) showed no C or N, and the lattice parameters do not match the tetragonal nitrides that might form in this material. Electron Energy Loss Spectroscopy (EELS) is generally better at detecting light elements and is currently planned to determine whether or not this phase is a nitride or a carbonitride.

Initial TEM analyses on samples aged at 649 and 704°C (Figure 6) suggest that the sample aged at 649°C is similar to that aged at 593°C with more precipitation mainly near the grain boundaries, and the sample aged at 704°C appears to be similar to that aged at 760°C. The long thin grain boundary precipitate in Figure 6 (left) has not yet been identified. The smaller precipitates are highly faulted and are most likely μ phase since internal twinning is characteristic of μ [5,6].

DISCUSSION

The microstructures resulting from aging are consistent with what was seen by Leonard [2] in C-276. At lower temperatures, a uniform film forms along the grain boundaries while at higher temperatures, the grain boundary film consists of discrete particles. This observation together with the internal faulting of the grain boundary film suggest that the uniform film formed by aging at 593°C is μ.



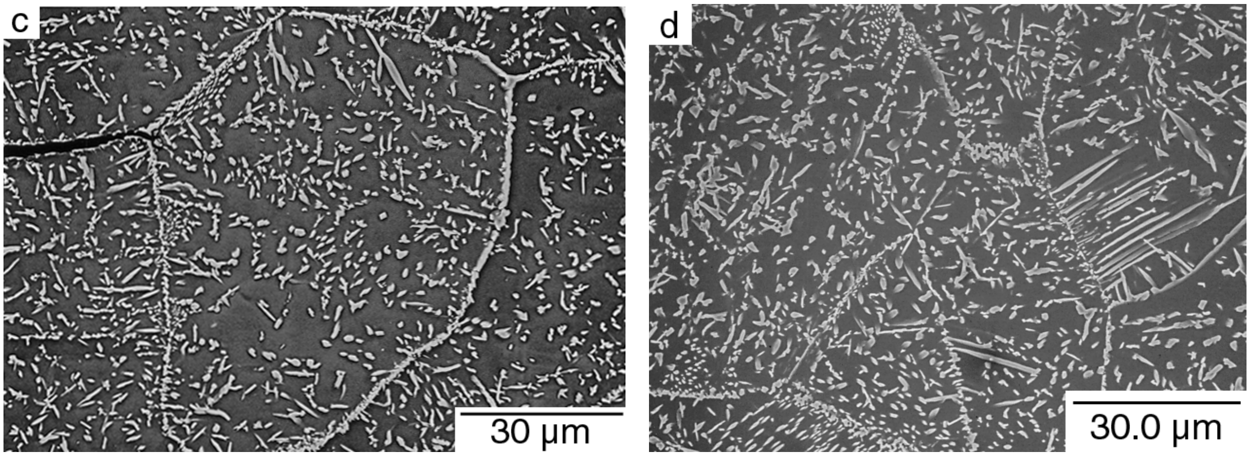


Figure 4. SEM micrographs of C-22 aged 16,000 h at a) 593°C, b) 649°C, c) 704°C and d) 760°C. The micrograph in (c) was taken near the fracture surface of a Charpy impact specimen and shows a secondary crack along the grain boundary. This grain boundary cracking was typical for these samples.

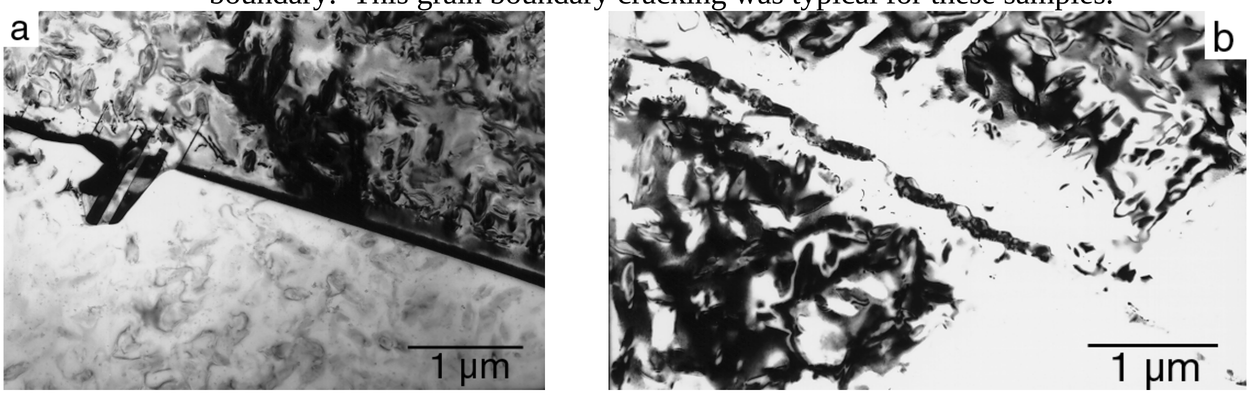


Figure 5. TEM micrographs of C-22 aged 16,000 h at 593°C. In some cases, (a), a thin, uniform grain boundary film forms, and in others, (b), the grain boundary film consists of discrete particles. Also, seen in (a), an as-yet unidentified phase is growing out of the grain boundaries.

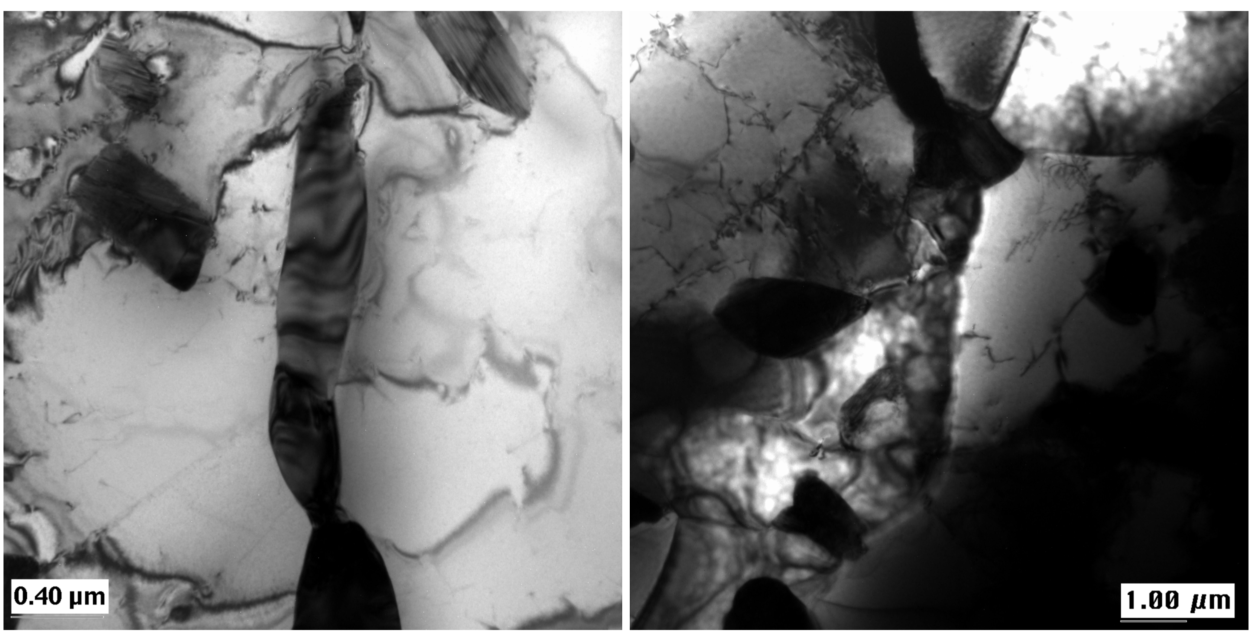


Figure 6. TEM micrographs of C-22 aged 16,000 h at 704°C (left) and 760°C (right).

The amount of strengthening was highest when the sample was aged at 704°C. This temperature is higher than the temperature at which the peak strengthening was seen by Matthews (about 590°C) [10]. The strengthening is thus most likely due to the formation of the rather hard μ phase rather than the ordered $Ni_2(Cr,Mo)$ phase as was the case for alloy S and alloy C-4 studied by Matthews. This is consistent with the results of Rebak et al. [7] who found very little strengthening with the ordering reaction in C-22.

The ductility of C-22 was drastically affected by the precipitation of μ in this study as it was in similar alloys [6,10]. It is difficult to say how much of the embrittlement is due to the formation of μ and how much is due to $Ni_2(Cr,Mo)$ since both will reduce ductility, and both are most likely present even at aging temperatures as low as 593°C. In all cases, the grain boundaries are almost completely covered by μ or some other nonmetallic phase. This grain boundary decoration is most likely responsible for the low Charpy impact values after aging for 16,000 h at all temperatures investigated. The lowest ductility values were seen at the higher aging temperatures when only μ phase was seen. The tensile elongation is less sensitive to grain boundary precipitation, and the precipitation of $Ni_2(Cr,Mo)$ likely plays a greater role in the reduction of the elongation than it does the Charpy impact toughness at the lower aging temperatures.

CONCLUSIONS

Aging at temperatures between 593 and 760°C for 2000 and 16,000 h resulted in strengthening of C-22 alloy. The greatest strengthening occurred after aging for 16,000 h at 704°C. No evidence of ordering was seen at this temperature, and the strengthening is believed to be due to the formation of the hard but brittle intermetallic μ phase. Strengthening of the alloy was accompanied by a decrease in ductility. Both μ and the ordered $Ni_2(Cr,Mo)$ phase have been shown to decrease ductility in these alloys. In this case, however, the grain boundaries are almost completely decorated with μ and, to a lesser extent, other nonmetallic phases at all aging temperatures investigated. This grain boundary precipitation is likely responsible for the decreased Charpy impact toughness after aging. Precipitation of the ordered $Ni_2(Cr,Mo)$ phase probably plays a greater role in the reduction of the total elongation seen in uniaxial tension testing of samples aged at temperatures below 600-650°C.

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